

Charge-carrier Spectra in Semiconducting Nanowire Functionalized by Incommensurate Molecular Structures

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Abstract

Functionalization of a semiconductor nanowire has been investigated by thin molecular layer which forms misfit dislocations. The way is shown that how it causes the electron spectra tuning. The self-consistent system of equations is derived. The system describes a charge carrier quantization in a semiconductor nanowire, incommensurate molecular structure, interaction of extra carrier in a nanowire, and molecular electric dipoles. The misfit dislocations create periodic quantum barriers for electrons that are relatively narrow and quantum wells for holes simultaneously. Change of the dislocation type or the dipoles orientation leads to mutual transformation of the hole and electron spectra. In turn, the carrier leads to the dislocation rearrangement. The misfit layer reconstructs nanowire electron superlattice spectra and creates different conditions of localization or tunnelling for holes and electrons dependent on orientation of the molecules.

Keywords

Nanowire; Nanotube; Functionalization; Misfit Dislocation; Schrodinger Equation

Introduction

The optical properties and conductance of a nano object are determined by the set of quantum energy levels of its charge carriers (see Agraita et al 2003, Ferry & Goodnick 1997). It has been observed for metal nanowires (Yanson et al 2001) and carbon nanotubes (CNTs) (Orlikowski et al 2001). CNTs are nanomaterials with a small diameter of about 1 nm, length of about 1 μ m and the mean free path of the charge carriers that exceeds 10 μ m which is important for quantization along CNT axis (Dekker 1999). In these articles, CNTs and nanowires have been considered as a quantum dot.

Functionalization, a new powerful method to tune CNTs quantum energy levels and keep their physical properties (Ciraci et al 2004, Daniel et al 2006), create the novel high-sensitive biosensors, electronic and optoelectronic devices. CNTs conductance is extremely sensitive to the presence of adsorbed molecules forming Langmuire-Blodgett films (Armitage, Gabriel, & Gruner 2004). Chips based on CNTs and DNA (Buzaneva et al 2002) or surface self-organizing organic structures (Neilands 2002) are discussed.

The theory of energy spectra tuned in the semiconductor nanowire (nanotube) as the result of functionalization by molecular films was developed (Lykah & Syrkin 2010). The different soft degrees of freedom have been considered in the molecular system: radial deformation (Lykakh & Syrkin 2005), conformation (Lykakh & Syrkin 2012), and misfit dislocations (the present work). The spectra are extremely sensitive to the state of the molecular subsystem. We investigated the interaction of the uncompensated charge (carried by an electron or a hole in a quantum nanowire) and the neighbouring medium that has low mechanical rigidity and consists of molecules in possession of intrinsic electric-dipole moment. The nonlinear nonlocal equations describing the system were derived for the system. Longitudinal quantization was reduced to the spectral problem for a nonlinear Schrodinger equation (Lykakh & Syrkin 2005) and to conformation domain quantization (Lykakh & Syrkin 2012). The shift of the charge-carrier energy levels and possibility of a carrier localization were calculated.

In this research, theoretical approach to the nanowire

spectra transformation has been developed as a result of functionalization by a thin molecular layer which forms misfit dislocations. The situation is expected when incommensurate molecular structure is formed along the nanowire. The incommensurate structure arises due to a competition of the molecules interaction in its own layer and with a nanowire as a substrate. The self-consistent system of equations includes (i) the time-independent Schrodinger equation for a charge carrier in a semiconductor; (ii) nonlinear equation of the Frenkel-Kontorova type for incommensurate molecular structure; (iii) the material equations for interaction of an extra carrier in nanowire and molecular electric dipoles subsystem; and (iv) the material equations for renormalization of molecules-substrate interaction when an extra carrier in nanowire exists.

Model of the System

Schrodinger Equation

The time-independent Schrodinger equation for an extra charge carrier in an intrinsic-semiconductor can be written as (see Ferry & Goodnick 1997, Landau & Lifshits 1980, Seeger 1989):

$$-\frac{\hbar^2}{2m_{ef}}\Delta\psi + U(\vec{r})\psi = W\psi \quad (1)$$

Here $\psi \equiv \psi(\vec{r})$, m_{ef} and \vec{r} are wave function, effective mass and radius vector of the carrier, respectively; Δ is Laplace operator, W is the total energy, $U(\vec{r})$ is the potential energy. Infinite depth well approximation is expressed as: $U(\vec{r}) \equiv U_0(\vec{r})$, where $U_0(\vec{r}) = 0$ inside and $U_0(\vec{r}) = \infty$ outside nanowire. On account of the interaction with the surrounding medium $U_{int}(\vec{r})$, the potential takes form:

$$U(\vec{r}) = U_0(\vec{r}) + U_{int}(\vec{r}) \quad (2)$$

In CNTs, Schrodinger equation takes matrix form (Ando 2005) and needs more careful approach.

Material Equation: Carrier-dipoles Interaction

This carrier-dipoles interaction can be relatively strong if functionalizing molecules have an intrinsic dipole moment \vec{d} . The electric-dipole moment in the organic molecules exists due to the presence of atomic groups that break the charge symmetry (Neilands 2002, Blinc & Žekš 1974). Summing up the contributions from all

the dipoles, one can get as a result the interaction potential energy $U_{int} = e\phi$ at a point \vec{r}_0 within the nanowire:

$$U_{int}^e(\vec{r}_0) = e \int d\vec{r}' n(\vec{r}') \vec{d}(\vec{r}') \frac{\vec{r}_0 - \vec{r}'}{\varepsilon |\vec{r}_0 - \vec{r}'|^3} \quad (3)$$

Here $n(\vec{r}')$ is the volume number density of the molecules, e is the carrier charge, $\vec{d}(\vec{r}')$ is the mean value of a dipole moment at the point \vec{r}' , and ε is the relative permittivity of the medium. In turn, the carrier charge determines the potential energy of the interaction with an individual molecular dipole:

$$U_{int}^d(\vec{r}') = -\vec{d}(\vec{r}') \int d\vec{r}_0 \frac{e |\psi(\vec{r}_0)|^2 (\vec{r}' - \vec{r}_0)}{\varepsilon |\vec{r}' - \vec{r}_0|^3} \quad (4)$$

(1-3) is set to be completed with following material equations

$$n(\vec{r}') = n(\vec{E}(\vec{r}')) \text{ or } n(\vec{r}') = n(U_s(\vec{r}')) \quad (5)$$

Here U_s is the substrate potential which influences the molecules. The interaction described by eqs. (3) and (4) is nonlocal and depends on the configuration of the system substantially. Schrodinger equation (1) with potentials (2-4) can be transformed into a nonlinear integro-differential equation which can be solved only by using methods of approximation (Landau & Lifshits 1980). In the experiments all the dimensions of CNT and the functionalizing layer are much smaller than the nanowire length, i.e. $r, R \ll 2L$ (see the photograph in (Armitage, Gabriel, & Gruner 2004)). In a cylindrical geometry, the separation of the coordinate variables is possible: $\psi(\vec{r}) = \psi(x)\psi_{\perp}(y, z)$ and $W = W_x + W_{\perp}$ (here, x is the coordinate along the wire axis). It is assumed as well that any variation in $\psi(x)$ occurs in a length of order L .

Approximation of a long nanowire allows the reduction of the integral contributions to those of a local nature. In cylindrical coordinates integral (3) has the integration limits r and R which coincide with the outer radii of the nanowire and the molecular layer correspondingly. In the absence of the charge carriers or in the case of a rigid molecular system, the density in (3-5) is constant ($n(\vec{r}') = n_0$) as well as \vec{d} and can be kept out of the integration sign. The integration over x (along nanowire axis) is reduced to the

integration with infinite limits, even for $x_0 - x' \geq 3R$.

The potential energy of a charge carrier interaction with the dipole subsystem is

$$U_{int}^{e0} = -4\pi n_0 de(R-r) \rightarrow -4\pi n_{s0} de. \quad (6)$$

Here n_{s0} is the surface density of the molecules in the limit case of the thin functionalizing layer.

The flux can be calculated instead of integral (4) to obtain an analytical expression for the potential energy. In other words, the local value of the radial field strength is replaced with a value for an infinitely long wire taking the local value of the wave function:

$$U_{int}^d(x) = -\frac{2\tau d}{\epsilon r'}; \quad (7)$$

$$\tau(x) = e |\psi(x)|^2 F_{\perp}; F_{\perp} = \int |\psi(y, z)|^2 dy dz.$$

Here $\tau(x)$ is local linear charge density. The positive direction of a dipole moment \vec{d} coincides with direction towards the centre of the nanowire as it is indicated by (3). The error in this result was estimated using the divergence theorem in (Lykakh & Syrkin 2005).

Frenkel-Kontorova Type Equation for Misfit Dislocation

Hamiltonian of a molecular chain on a substrate is (Davydov 1991, Braun & Kivshar 2004):

$$H_{FK} = \frac{1}{2} \sum_n [m \dot{u}_n^2 + \kappa (u_n - u_{n-1})^2 + U(u_n)]. \quad (8)$$

Here u_n is a displacement of a molecule in the n^{th} site from an equilibrium position in the chain and κ is an elastic constant for a relative molecular displacement. $U(u_n)$ is the potential that acts on the n^{th} molecule from the substrate.

$$U_s(u_n) = U_0 [1 - \cos(\frac{2\pi u_n}{a_s})]. \quad (9)$$

Here a_s is the substrate lattice constant. Hamiltonian (8) leads to discrete equation of motion:

$$m \ddot{u}_n + \kappa (2u_n - u_{n-1} - u_{n+1}) + \frac{\pi U_0}{a_s} \sin(\frac{2\pi u_n}{a_s}) = 0. \quad (10)$$

Continual approximation can be introduced with:

$$u_n(t) = u(x, t); \phi(x, t) = \frac{2\pi u(x, t)}{a_s} \quad (11)$$

$$U_s(\phi(x, t)) = U_0 [1 - \cos(\phi(x, t))];$$

Where ϕ is an effective phase? Then continual equation of motion is

$$\phi'' - \frac{1}{c_0^2} \ddot{\phi} = \frac{1}{\lambda_0^2} \sin \phi. \quad (12)$$

Here characteristic length and longitudinal sound velocity in molecular chain (layer) are

$$\lambda_0 = \frac{a_m^2}{2\pi} \sqrt{\frac{2\kappa}{U_0}}; c_0 = a_m \sqrt{\frac{\kappa}{m}} \quad (13)$$

Here a_m is the molecular subsystem lattice constant and $|a_m - a_s| \ll a_m \approx a_s$. The static solutions are in study. So equation (12) has integral E:

$$(\phi')^2 = \frac{2}{\lambda_0^2} (E - \cos \phi). \quad (14)$$

At $E=1$ the continual equation has stationary solution as solitary domain wall:

$$\phi(x) = 4 \arctan[\sigma \exp \frac{x - x_0}{\lambda_0}]. \quad (15)$$

In dependence on topological charge $\sigma = \pm 1$, this solution gives kink ($\sigma = +1$) or antikink ($\sigma = -1$) that is presented in Fig.1(a).

At $E > 1$, the continual equation of motion also has such periodic stationary solution:

$$\cos(\frac{\phi(x)}{2}) = -\sigma \text{sn}(\xi, k); \xi = \frac{x - x_0}{k \lambda_0} \quad (16)$$

Here $\text{sn}(\xi, k)$ is Jakobi elliptic function with elliptic module k defined by relation (Davydov 1991):

$$k^2 = \frac{2}{E+1}; 0 \leq k \leq 1 \quad (17)$$

The solution (16) can be rewritten in such form:

$$\phi(x) = 2 \sin^{-1}[\sigma \text{sn}(\xi, k)] + \pi \quad (18)$$

The period of $\text{sn}(\xi, k)$ in dependence on ξ is $4K(k)$. Here $K(k)$ is the full elliptic integral of the first kind. Following (Davydov 1991) in (16, 18), the space period in dependence on the variable x (and approximate expression) is

$$l_x = 4kK(k)\lambda_0 \approx \frac{2a_s^2}{|a_s - a_m|} \quad (19)$$

Using (19) one can evaluate the elliptic module k and then the integral E value from (17). At $k \rightarrow 1$ the integral has limit $K(k) \rightarrow \infty$. In the limit case $k \rightarrow 0$ or $E \rightarrow +\infty$ the periodic solutions (16, 18) can be presented as $\text{sn}(\xi, k) \rightarrow \sin(k\xi)$ that means homogeneous changing of displacement u_n in the molecular chain.

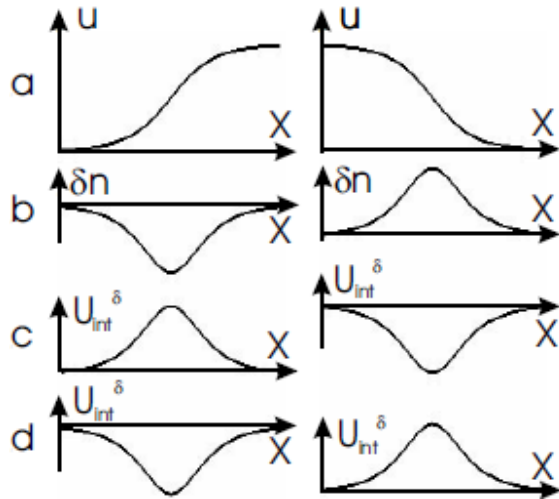


FIG. 1 a) THE FUNCTIONALIZING MOLECULES COORDINATES IN KINK (LEFT PANEL) AND ANTINK (RIGHT PANEL) DISLOCATION ACCORDING TO (15). b) CORRESPONDING CHANGING OF THE MOLECULE SURFACE DENSITY (21a). c) BAND EDGE MODULATED ACCORDING TO (22) AT DIPOLES ORIENTED TO NANOWIRE AXIS. d) THE BAND MODULATED EDGE AT DIPOLES ORIENTED FROM NANOWIRE AXIS

In the limit case $k \rightarrow 1$ or $E \rightarrow 1$ ($E > 1$) the periodic solution (16) can be presented as a set of solitary domain walls (15) with space period (19). One of these dislocations is shown in Fig.1. At $E = 1$ the space periods of the molecular layer and nanowire coincide. $n_s(x) = n_{s0}$ and a solitary dislocation is possible (15). Regions of local extension (kink, $\sigma = +1$) or constriction (antikink, $\sigma = -1$) exist where deviation of concentration is:

$$\delta n_s(x) = n_{s0} \frac{\partial u}{\partial x} \quad (20)$$

At $E > 1$ the space period of the molecule layer does not coincide with the nanowire substrate lattice constant, the functionalizing molecule displacement $u(x, t)$ and corresponding phase $\phi(x, t)$ grow continuously according to (16). The periodic misfit dislocations (16) arise in the molecular layer. Using

(15), (18) and (20) one can obtain analogies of bright or dark solitons:

$$\delta n_s(x) = \frac{n_{s0} a_s}{\pi \lambda_0} \begin{cases} \sigma \text{sech}(\frac{x}{\lambda_0}); E = 1 \\ \frac{\sigma}{k} \text{dn}(\frac{x}{k\lambda_0}, k); E > 1 \end{cases} \quad (21)$$

Then the potential U_{int}^{e0} (6) can be transformed into

$$U_{int}^e(x) = U_{int}^{e0} + U_{int}^{e\delta}(x) \quad (22)$$

$$U_{int}^{e\delta}(x) = -4\pi de \delta n_s(x)$$

The integration along the nanowire axis on misfit period yields $\Delta n_s = \sigma a n_{s0}$ with extra ($a_s < a_m, \sigma = -1$) or lack ($a_s > a_m, \sigma = +1$) row of the molecules. The creation of partial dislocations is very probable on account of relatively big size and complicated construction of organic molecules.

Renormalization of Interaction with Substrate

Material equation for the renormalized interaction of the molecular layer with the substrate has to account on the effect of the substrate U_s and the carrier charge field (7) potentials simultaneously:

$$U_s^d(z, x) = U_s(z, x) + U_{int}^d(z, x) \quad (23)$$

Here x and z are coordinates along the nanowire and along its radius correspondingly, $U_s(z) = U_{si}(z)$ at incommensurate and $U_s(z) = U_{sc}(z)$ at commensurate regions. Radial equilibrium position of a molecule can be found from $\partial U_s(z, x) / \partial z = 0$ for neutral nanowire. Then the substrate potential (9) can be written as

$$U_s(z_0, x) = U_0(z_0) [1 - \cos(\frac{2\pi u(x)}{a})] \quad (24)$$

Here the amplitude of the substrate potential can be found through the interaction potentials in incommensurate and commensurate fragments:

$$U_0(z_0) \rightarrow U_0(z) = \frac{1}{2} [U_{si}(z) - U_{sc}(z)]. \quad (25)$$

In relation (24) the zero level of the potential is chosen for commensurate fragments with further (stronger) interaction. Incommensurate fragments have relatively weak interaction with the substrate. A depth and a rigidity of the interaction energy are higher for the

commensurate fragments of the adsorbed phase correspondingly. Then the expansion of the potential of the molecular interaction with the substrate near the equilibrium position z_0 depends on the rigidity k_s :

$$U_s(z_0 + \delta) = U_{0s}(z_0) + U_{2s}(z_0, \delta)$$

$$U_{2s}(z_0, \delta) = \frac{k_s(z_0)}{2} \delta^2; k_s(z) = \frac{\partial^2}{\partial z^2} U_{0s}(z) \quad (26)$$

Here δ is deviation from z_0 . The commensurate fragments are more rigid: $k_{sc}(z_0) > k_{si}(z_0)$

In case of a nanowire with a carrier, the molecule equilibrium position is determined by condition $\partial U_s^d(z, x) / \partial z = 0$. On account of relations (26) for $U_s(z_0 + \delta, x)$ and (7) for $U_{int}^d(z, x)$, the equilibrium elastic displacement of an individual dipole pulled into (or pushed out of) the region of a stronger field can be found in harmonic approximation:

$$\delta = - \frac{2\tau d}{k_s(z, x) \epsilon r'^2} \quad (27)$$

Substitution of δ into Eq. (23) and accounting of (26) and (7) give the potential energy of elastically displaced dipoles in the field of a charge carrier: $U_s^d(z, x) = U_s(z, x) + U_{int}^d(z, x)$. Here the interaction with the substrate can be expanded: $U_s(z_0 + \delta, x) = U_{0s}(z_0, x) + U_{2s}(z_0, x, \delta)$ where

$$U_{2s}(z_0, x, \delta) = G_4 |\psi(x)|^4 \quad (28)$$

$$G_{4s} = \frac{2}{k_s(z_0, x)} \left[\frac{deF_{\perp}}{\epsilon r_0'^2} \right]^2 \quad (29)$$

The inequality $G_{4sc} < G_{4si}$ is obtained by accounting of relation between rigidity. The interaction of the molecules with a charge carrier can be expanded as

$$U_{int}^d = U_{int0}^d + U_{int1}^d$$

$$U_{int0}^d(x) = -G_2 |\psi(x)|^2;$$

$$U_{int1}^d(z_0, x) = -2G_{4s} |\psi(z_0, x)|^4; \quad (30)$$

$$G_2 = \frac{2deF_{\perp}}{\epsilon r_0'} \quad (31)$$

Finally, the simultaneous effect of the substrate and carrier charge field potentials came into effect:

$$U_s^d(z, x) = U_{s0}(z_0, x) - G_2 |\psi(x)|^2 - G_{4s} |\psi(x)|^4 \quad (32)$$

Then on account of relation (29), the amplitude of the substrate potential can be found through the interaction potentials in incommensurate $U_{si}(z_0, x)$ and commensurate $U_{sc}(z_0, x)$ fragments in (32):

$$U_{0E}(z_0, x) = U_0 - \delta G_{4s} |\psi(x)|^4 < U_0$$

$$\delta G_{4s} = \left[\frac{1}{k_{si}(z_0)} - \frac{1}{k_{sc}(z_0)} \right] \times \left[\frac{deF_{\perp}}{\epsilon r_0'^2} \right]^2 \quad (33)$$

After substitution of (33) into (11) the Frenkel-Kontorova potential renormalized by a carrier electric field has been obtained. In this case terms $\sim |\psi(x)|^2$ are compensated. Long wave modulation along Ox axis appears $\sim |\psi(x)|^4$, according to (19) and (13) we get $l_{xE} \sim \lambda_{0E} \sim 1/\sqrt{U_{0E}}$. On account of $U_{0E} < U_0$ and (33) we have $l_{xE} > l_x$.

On account of a nonlinear characteristics of the molecule-substrate interaction (sharp repulsion and soft attraction), one can calculate more rigid repulsion and soft attraction. The obtained result does not depend on a concrete form of the interaction qualitatively.

Results

Superlattice by the Misfit Dislocations

Let us consider an action of the functionalizing layer on a carrier inside the nanowire. With this purpose the electric potential has been calculated created by the functionalizing molecules. In this case the Schrodinger equation (1) can be rewritten in order to describe one dimensional motion of the charge carrier in the nanowire as follows:

$$-\frac{\hbar^2}{2m_{ef}} \frac{\partial^2 \psi(x)}{\partial x^2} + [U_0(x) + U_{int}^{e0}(x) + U_{int}^{e\delta}(x)] \psi(x) = W_x \psi(x) \quad (34)$$

Here $-L < x < +L$. The initial potential equals inside $U_0(x) = 0$ and outside $U_0(x) = \infty$ of this interval.

The potential U_{int}^{e0} given by relation (6) is responsible for a homogeneous shifting of the bottom of the quantum well. The potential $U_{int}^{e\delta}(x)$ given by relations (21, 22) is responsible for creation of a

superlattice structure in case of a periodic dislocation arrangement. The inequalities $\lambda_0 \ll l_x \ll L$ have to be satisfied. At $E > 1$ the periodic potential $U_{int}^{e\delta}(x)$ can be transformed into the form

$$U_{int}^{e\delta}(x) = 4n_{S0}de \frac{\sigma a_s}{k\lambda_0} dn\left(\frac{x}{k\lambda_0}, k\right) \quad (35)$$

Band structure modulation of the semiconducting nanowire at $E > 0$ and $\sigma d > 0$ is shown in Fig.2. It is a set of the dislocation potentials shown in left column of Fig.1(c) or right column of Fig.1(d) with narrow barriers for electrons in the conductivity band. The valence band top has narrow peaks.

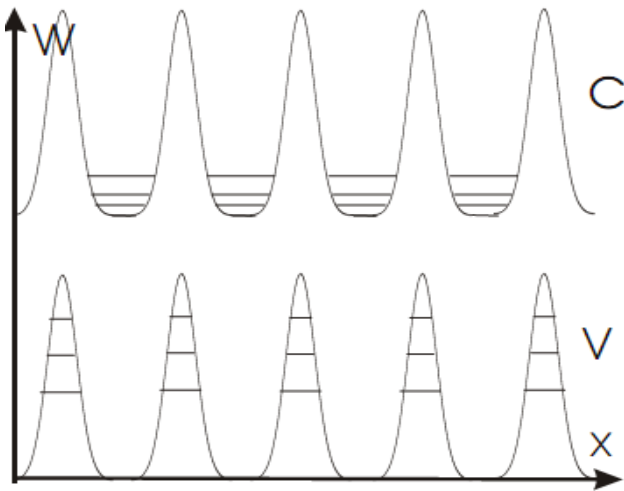


FIG. 2 THE MODULATED BAND STRUCTURE OF SEMICONDUCTING NANOWIRE ACCORDING TO (22). QUANTUM LEVELS OF ELECTRONS IN CONDUCTIVITY BAND (C) AND HOLES IN A VALENT BAND (V) ARE SHOWN

The periodic quantum barriers for electrons are relatively narrow and can form the superlattice carrier spectrum. Let us consider strong and weak coupling approximations.

1) Strong Coupling Approximation

The lowest quantum levels for electrons (between relatively narrow barriers in the conductivity band) and holes (between relatively wide barriers in the valence band) are shown in Fig.2 qualitatively. The hole quantum levels have considerably higher intervals than the electron levels as the sequence of narrower quantum well.

The band structure modulation at $E > 0$ and $\sigma d < 0$ can be obtained from Fig.2 by mirror reflection about the axis Ox. The potential is to be taken from the right column Fig.1(c) or the left column Fig.1(d) with narrow wells for electrons in conductivity band, when the valence band top for holes has narrow barriers.

2) Weak Coupling Approximation.

The space periods are the lattice constant a and the superlattice constant l_x defined by equation (19). In the reciprocal space, corresponding periods are $2\pi/a$ and $2\pi/l_x$. Corresponding Brillouin zone boundaries are located at π/a for the lattice and $k_{pSL} = \pi/l_x$ for the superlattice.

In common semiconductor, a parabolic dispersion law is symmetric relative to quasimomentum value $k_p = 0$ where minimum or maximum is arranged. The CNT specific is the arrangement of the dispersion law extremes in the points $\pm k_0 \neq 0$ (Endo et al 1996). The very similar situation is observed in common many-valley semiconductors (Seeger 1989).

The electronic minigap spectrum in the vicinity of the point $+k_0$ may have different positions, see Fig.3. Asymmetric arrangement around the minimum is general for the superlattice minigaps of the electronic spectrum in the vicinity of the point $+k_0$. It is common relative position of the dispersion curve and the superlattice Brillouin zone boundary (minigap). Each minigap corresponds to forbidden values of electron energy; nevertheless, another branch of a parabolic spectrum has the same allowed values of energy, which means that all values of the electron energy are allowed and the spectrum has a quasi gap which can be transformed into observed minigaps if the energy distance between the minigap centres does not exceed the widths of the coincided gaps. The hole spectrum can be obtained from mirror reflection about the horizontal axis.

Symmetric arrangement of the superlattice gaps around the minimum is shown in Fig.3(b) and Fig.3(c). It is possible for the following special values:

$$k_{pSL} = \begin{cases} \frac{2k_0}{2n+1}; \text{Fig } b \\ \frac{k_0}{n}; \text{Fig } c \end{cases} \quad (36)$$

where n is an integer. In these cases both branches

of the parabolic dispersion law have the same forbidden energy values. The superlattice mini gaps can be observed with different physical characteristics, first of in which is optic spectra and conductivity.

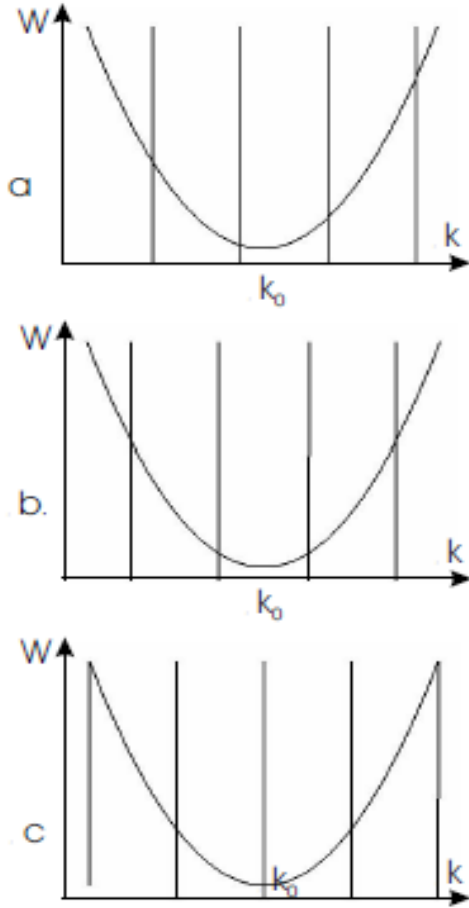


FIG. 3 ELECTRON BRANCH OF THE DISPERSION LAW IS SHOWN NEAR THE MINIMUM POINT IN A SEMICONDUCTING NANOWIRE MODULATED AS THE SUPERLATTICE DUE TO THE MISFIT DISLOCATIONS. a) ASYMMETRIC AND b), c) SYMMETRIC ARRANGEMENT OF THE SUPERLATTICE GAPS ABOUT THE MINIMUM

Selfconsistence. Misfit Dislocation Rearrangement. Carrier Localization.

A carrier inside a nanowire in turn creates an action on the functionalizing molecular layer. The amplitude of the substrate potential has been found in (33). Substitution of (33) into (11) gives the Frenkel-Kontorova potential with the amplitude renormalized by a carrier electric field. According to these relations, the long wave modulation along Ox axis occurs $\sim |\psi(x)|^4$. A carrier attracts (repulses) the molecular layer that leads to the widening of coherent regions and dislocation rearrangement. On accounting of (33), the characteristic length (13) in molecular chain (layer) takes such form:

$$\lambda_{0E}(x) = \frac{a^2}{2\pi} \sqrt{\frac{2\kappa}{U_{0E}(x)}} \approx \lambda_0 \left[1 + \frac{\delta G_{4s} |\psi(x)|^4}{2U_0} \right] \quad (37)$$

In relations (19), the space period of misfit dislocation turns to dependence on the carrier electric field $l_{xE}(x) \sim \lambda_{0E}(x)$.

Then higher carrier density inside the nanowire creates regions with larger space period of the misfit dislocation. Direct inserting (37) with the function which has one maximum (probe function $\psi \sim \cos(\pi x / 2L)$) into (18) and (21b) yields the qualitative picture of the dislocation rearrangement and band modulation that is presented in Fig.4(b). This physical situation is realized only if the extra electron in nanowire exists quite long time for the misfit dislocation redistribution. It looks like the dislocation rearrangement is absent from realization completely. The reason is that the superlattice tunnelling is destroyed and the electron turns to being locked in one period of the deformed dislocation structure at the first changing of the dislocation periodicity.

In the case of fast tunnelling of a carrier, the dislocations have no time to move, thus the undisturbed picture in Fig.4 (a) and the superlattice spectrum is kept unchanged.

The periodic quantum wells for a hole in a nanowire are relatively narrow and divided into wide commensurate regions. There is a strong probability that the carrier localization at a dislocation is shown in Fig.4(d). The dislocation width and the potential depth change to provide a minimum energy of the system hole-dislocation. In cases b, c and d, the dislocation system shift is overstated for convenient illustration.

The case $E > 1$ and $\sigma d > 0$ are shown in Fig.2 and Fig.4, respectively. In case of $\sigma d < 0$, Fig.2 and Fig.4 are to be reflected about the horizontal axis as a mirror. Then all the results of the investigation on the hole are applied to an electron and vice versa.

To estimate the electron or the changing hole potential due to the molecules, the values for the parameters are employed following (Lykakh & Syrkin 2005, Davydov 1991, Blinc & Žekš 1974). Thus, equation (6) allows evaluating the change of the bottom level of the

quantum well in a nanowire with functionalizing molecular layer: $|U_{int}^{e0}| \sim (1 \div 10) \text{ eV}$. The barrier height can be evaluated as

$$|U_{int}^{e\Delta}(x)| \sim |U_{int}^{e0}| a / \lambda_0 \sim (0.01 \div 1) \text{ eV}.$$

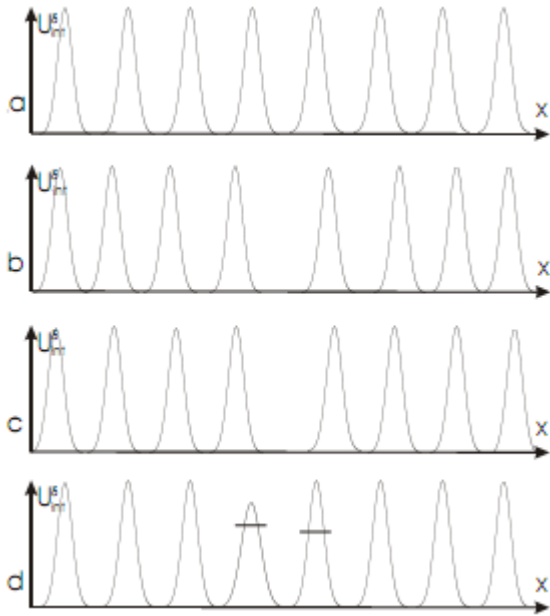


FIG. 4. FORM OF THE CONDUCTING BAND BOTTOM OR VALENCE BAND TOP

A) HOMOGENEOUS MISFIT DISLOCATION DISTRIBUTION ALONG A NANOWIRE AS IN FIG.2

B) THE FIRST STAGE OF REARRANGEMENT OF THE MISFIT DISLOCATION IN THE ELECTRON ELECTRIC FIELD

C) THE FINAL STAGE IS LOCALIZATION AT ONE DISLOCATION PERIOD

D) HOLE LOCALIZATION ABOUT A PEAK OF VALENCE BAND TOP AT ONE DISLOCATION. HORIZONTAL LINES MARK THE HOLE LEVEL SHIFT AT LOCALIZATION

Conclusions

The following physical results are obtained.

- (i) The molecule-substrate (nanowire) interaction orients the molecules and their intrinsic dipole moments related to the substrate surface.
- (ii) The periodic system of misfit dislocations of the functionalizing molecules exists at the nanowire surface under certain conditions. These misfit dislocations may be of two kinds: with or without interstitial molecular row. They are analogies of bright or dark solitons. The periodic dislocations are divided into wide commensurate regions.
- (iii) A homogeneous distribution of the molecular dipoles creates a homogeneous shift of electric potential along the nanowire. The periodic misfit

dislocations with extra or lack dipoles create a superlattice potential for a carrier inside the nanotube. A set of quantum wells and barriers arises and modulates a band edge. The created potential relief depends on orientation of the dipoles and the kind of misfit dislocation. The topological invariant $\text{sign}(\sigma d) = \pm 1$ defines the creation of the relatively narrow peaks or wells for electron (correspondingly the wells or peaks for hole).

(iv) The periodic modulation of the nanowire band structure due to the molecular layer dislocation forms the superlattice carrier spectrum for either an electron or a hole. The misfit dislocations create the same periodic relief of the valence and conductivity bands edges. Considerable deviation of the reliefs of the band edges from a sinusoidal function breaks this symmetry of the spectra. The narrow peaks are easily penetrated by a carrier that makes the narrow gap or quasi gap arise in corresponding band. In another band, the narrow wells are divided into wide barriers then tunnelling is rather difficult, which causes very narrow mini band or a set of the split quantum levels; and localization is also possible.

(v) The charge of the carrier attracts the molecular layer that breaks the periodicity of dislocations' arrangement. The coherent regions expanding with the increment of the carrier charge density, destroys mini band structure and can speed up the carrier localization. The carrier localization on a single peak causes adjustment of dislocation structure. At longitudinal quantization, the effect on the walls of the potential well vanishes under localization condition. The energy becomes independent on the nanowire length L but depends on the dislocation width λ_{0E} or dislocation period l_{xE} as it is shown in Fig.4 where $\lambda_{0E} \ll l_{xE} \ll L$. This scenario works only under presence of the carrier in nanowire for a long time.

(vi) In the nanowire, the spectra of holes and electrons are symmetric. The layer of the functionalizing molecules with the intrinsic electric dipoles breaks this symmetry. This dipoles layer creates opposite conditions for carrier localization or tunnelling along the dislocation superlattice in dependence on a charge sign, the dipoles orientation, and a kind of dislocation.

(vii) The misfit dislocation system of the functionalized nanowire and the induced superlattice spectra are extremely sensitive to variation of the molecule-molecule and molecule-substrate interaction

constants. It may be caused by temperature, phase transitions, filling of functionalizing layers and impurity. The high rigidity of the functionalizing molecular system leads to decrement of the dislocation concentration and suppression of the localization in the superlattice spectrum. The nanowire conductivity in these cases should grow significantly. Thus, a nanowire can be used as a sensor for the state of the molecular system.

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